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Communication

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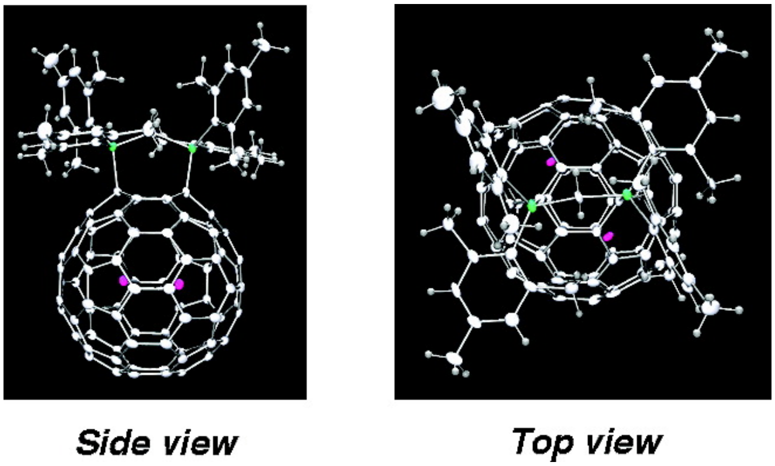

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Positional Control of Encapsulated Atoms Inside a Fullerene Cage by Exohedral Addition

Michio Yamada,[†] Tsukasa Nakahodo,[†] Takatsugu Wakahara,[†] Takahiro Tsuchiya,[†] Yutaka Maeda,[‡]
Takeshi Akasaka,*[,†] Masahiro Kako,[§] Kenji Yoza,*[,¶] Ernst Horn,[#] Naomi Mizorogi,[£]
Kaoru Kobayashi,[£] and Shigeru Nagase*[,£]

Center for Tsukuba Advanced Research Alliance, University of Tsukuba, Tsukuba, Ibaraki 305-8577, Japan, Department of Chemistry, Tokyo Gakugei University, Koganei, Tokyo 184-5801, Japan, Department of Applied Physics and Chemistry, The University of Electro-Communications, Chofu, Tokyo 182-8585, Japan, Bruker AXS K.K., Yokohama, Kanagawa 221-0022, Japan, Department of Chemistry, Rikkyo University, Tokyo 171-8501, Japan, and Department of Theoretical Molecular Science, Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan

Received June 30, 2005; E-mail: akasaka@tara.tsukuba.ac.jp; nagase@ims.ac.jp

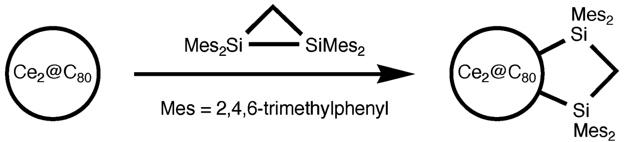
Up to now, many endohedral fullerenes (fullerenes with atoms encapsulated inside hollow carbon cages) have been prepared and isolated.[1,2] Control of motion of atoms within a cage is expected to be very valuable in designing functional molecular devices with new electronic or magnetic properties.[3,4] In 1997, we reported the three-dimensional random motion of two La atoms in $La_2@C_{80}$.[5] If the electrostatic potential inside the cage can be changed, it is possible to control the motion of encapsulated metal atoms. In this context, one plausible way may be to attach a molecule on the outer surface of the cage.[6] So far, no experimental evidence for manipulation of the motion of "untouchable" metal atoms inside the fullerene cage has been reported. We report here for the first time that the circular motion of metal atoms inside the fullerene cage is controllable by exohedral chemical functionalization. This helps in designing and regulating novel supramolecules with new electronic and structural properties, which encapsulates atoms or a molecule inside the spheroidal architecture cage.

The first isolation of $Ce_2@C_{80}$ was reported by Yang and coworkers in 1996.[7] It is suggested that each Ce atom in $Ce_2@C_{80}$ donates three valence electrons to the carbon cage, providing a stable closed-shell electronic structure on C_{80}, as in the case of $La_2@C_{80}$. However, the structural determination of $Ce_2@C_{80}$ has not been carried out yet. Therefore, we first measured the ^{13}C NMR spectrum of $Ce_2@C_{80}$ to determine its structure in CS_2 at 298 K. The ^{13}C NMR spectrum shows only two signals at 148.6 and 124.7 ppm with a 3:1 intensity ratio, respectively. This suggests that two Ce atoms circulate freely inside the I_h symmetrical C_{80} cage, as do two La atoms in $La_2@C_{80}$.[5]

Recently, we have found that the three-dimensional random motion of two La atoms in $La_2@C_{80}$ could be restricted to the circular motion in a plane by attaching an electron-donating molecule, such as disilirane, on the outer surface of the C_{80} cage.[8] To see how electronic properties can be changed by attaching an electron-donating molecule, density functional calculations have been carried out for $La_2@C_{80}(H_2Si)_2CH_2$. It was calculated that a considerable charge transfer takes place from the disilirane part to $La_2@C_{80}$, giving an electronic structure described as $(La_2@C_{80})^{-0.9}$-$((H_2Si)_2CH_2)^{+0.9}$.

A toluene solution of $Ce_2@C_{80}$ and 1,1,2,2-tetrakis(2,4,6-trimethylphenyl)-1,2-disilirane was heated at 80 °C for 4 h to afford the silylated adduct **1** (Scheme 1), which can be readily isolated by the preparative HPLC. The formation of **1** was confirmed by mass spectroscopic measurement. Mass spectrometry of **1** displays a parent peak at *m*/*z* 1786 as well as a peak for $Ce_2@C_{80}$ at *m*/*z* 1240 that arises by the loss of the disilirane part from **1**. The structure of **1** was fully determined by ^{1}H, ^{13}C, ROESY, and HMBC NMR spectroscopic and X-ray crystallographic analyses.

Scheme 1



1

The vis−near-IR absorption spectrum of **1** in toluene shows an absorption maximum at 819 nm, whereas that of $Ce_2@C_{80}$ exhibits a featureless absorption. Such a large difference in the absorption spectrum between pristine $Ce_2@C_{80}$ and **1** is ascribed to the change of the electronic structure of the cage, which is caused by the electron donation from the silyl substituent to the cage. The electronic property of **1** has been clarified by cyclic (CV) and differential pulse voltammetry (DPV) measurement in 1,2-dichlorobenzene using $(n\text{-Bu})_4NPF_6$ as a supporting electrolyte. As compared to $Ce_2@C_{80}$, both oxidation and reduction potentials of **1** were cathodically shifted to 640 and 340 mV, respectively. This result reveals that silylation is strongly effective for electron donation from the substituent to the cage.

The ^{1}H NMR spectrum of **1** shows two sets of 11 signals in a 6:1 ratio at 193 K. The change of its ratio upon increasing the temperature suggests that each set of signals originates from two conformers (the major (**1-A**) and minor (**1-B**) conformers).[9] The ROESY NMR measurement has been carried out to analyze an interconversion between **1-A** and **1-B** in more detail.[9] The exchange cross-peaks between **1-A** and **1-B** were observed in methyl, methylene, and meta-protons at temperatures ranging from 293 to 233 K. These exchange cross-peaks corresponding to an interconversion between **1-A** and **1-B** entirely disappeared at 193 K, which suggests that the chemical exchange is slower than the NMR time scale (mixing time = 200 ms). This result suggests that the interconversion between **1-A** and **1-B** is derived from the conformational change of the disilirane part. The ^{13}C NMR spectrum of **1-A** at 283 K shows a total of 59 signals involving 40 signals for the C_{80} skeleton.

A total of 12 signals derived from four tertiary and eight quaternary aromatic carbon atoms, six methyl carbon atoms, and

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[†] University of Tsukuba.
[‡] Tokyo Gakugei University.
[§] The University of Electro-Communications.
[¶] Bruker AXS K.K.
[#] Rikkyo University.
[£] Institute for Molecular Science.

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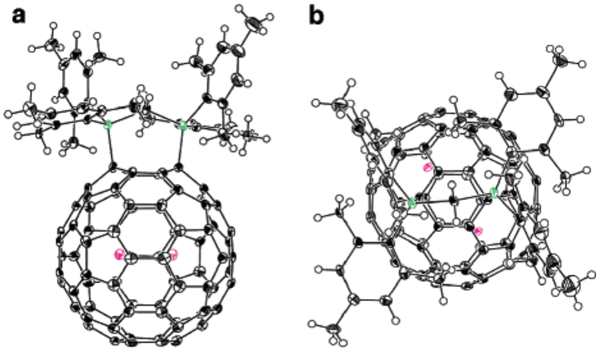

Figure 1. (a) Side view and (b) top view of the ORTEP drawings of **1-A** at 90 K. Thermal ellipsoids are shown at 50% probability level. The CS_2 molecules are omitted for clarity.

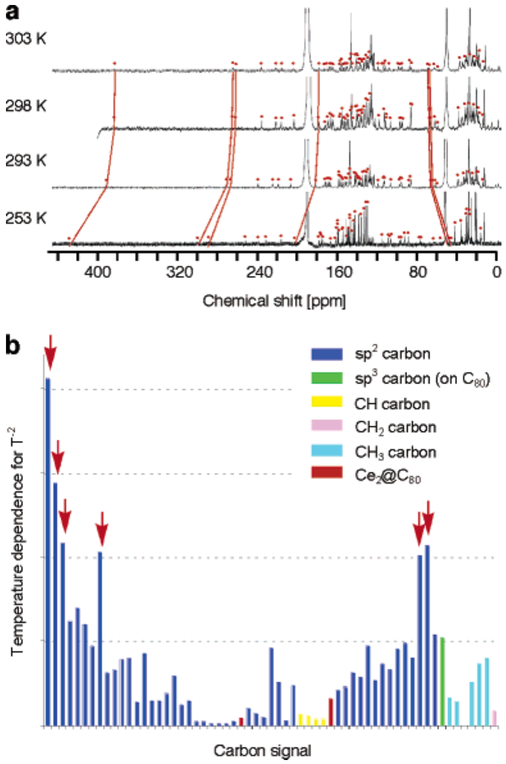

Figure 2. (a) ^{13}C NMR spectra of **1** at 253−303 K and (b) the temperature dependence for T^{-2}. Carbon signal lines in order of chemical shifts at 298 K. The red arrows show the carbon signals that are strongly affected by paramagnetic effect.

one signal for the methylene carbon atoms of the disilirane part were also observed. The HMBC NMR spectrum shows one cross-peak corresponding to the methylene proton and one sp^3 carbon atom of C_{80}, also indicating that **1-A** has C_2 symmetry. On the other hand, the relative intensity of **1-B** was too small to observe the ^{13}C signals.

The X-ray crystal structure of **1** shows two kinds of conformers as disorder derived from the disilirane part, which correspond to **1-A** and **1-B** found by ^1H NMR spectrum.[10] Figure 1 shows only the major conformer (**1-A**) for clarity. It is noteworthy that two Ce atoms now stand still at two positions at the equator of **1-A**.[11]

To clarify the motion of two Ce atoms in solution, ^{13}C NMR spectral analysis was carried out by varying temperatures.[12] It is noteworthy that only six signals out of a total of 59 ^{13}C signals are highly shifted by decreasing temperatures from 303 to 253 K, as shown in Figure 2. This can be explained only with the fact that each Ce atom is directed toward a hexagonal ring at the equator of the C_{80} cage, as found in the X-ray crystal structure, because the signals of the sp^3 carbon atoms at the two poles are not significantly shifted by the paramagnetic effects of the *f*-electron on Ce.[12]

In conclusion, an exohedrally functionalized derivative (**1**) of $Ce_2@C_{80}$ was successfully synthesized and fully characterized. The X-ray crystallographic and NMR spectroscopic analyses reveal that the free random motion of two Ce atoms in $Ce_2@C_{80}$ is fixed at specific positions by exohedral chemical functionalization. It is noteworthy that attachment of a silicon substituent can regulate the position of metal atoms under the equator inside the carbon cage. This is the first experimental evidence for control of the motion of encapsulated atoms inside the fullerene cage. One may expect that chemical functionalization can settle the position of metal atoms under the equator or at the pole-to-pole plane inside the cage. Such control of the motion of metal atoms by chemical functionalization is expected to be of great help in designing novel molecular devices with new electronic or magnetic properties.

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Supporting Information Available: Complete refs 6 and 12, preparation and spectroscopic data of $Ce_2@C_{80}$ and **1**, and ORTEP drawing of **1-B**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) $\Delta G^{\ddagger}$ = ca. 12 kcal/mol and ΔG = ca. 0.8 kcal/mol for the interconversion from **1-A** to **1-B** obtained by ROESY and ^1H NMR measurements, respectively.

(10) Black crystals of **1** were obtained by slow evaporation of the solution in mixed solvent of CS_2 and dichloromethane. Single-crystal X-ray diffraction data were collected on a Bruker SMART APEX equipped with a CCD area detector using Mo Kα radiation in the scan range $1.11° < \theta < 26.37°$. Crystal data of $1{\cdot}3(CS_2)$: $C_{120}H_{46}Ce_2S_6Si_2$, $M_W = 2016.35$, orthorhombic, space group $P2_12_12_1$, $a = 11.2325(6)$ Å, $b = 23.7339(13)$ Å, $c = 28.7821(16)$ Å, $\alpha = \beta = \gamma = 90.00°$, $V = 7673.0(7)$ Å^3, $Z = 4$, $D_{calc} = 1.745$ Mg/m^3, $\mu = 1.429$ mm^{-1}, $T = 90$ K, crystal size 0.42 × 0.10 × 0.05 mm^3; 89 123 reflections, 15 678 unique reflections; 11 990 with $I > 2\sigma(I)$; $R_1 = 0.0432$ [$I > 2\sigma(I)$], $wR_2 = 0.1079$ (all data), GOF (on F^2) = 1.004. The maximum residual electron density is equal to 0.826 e Å^{-3}.

(11) The docking position of two Ce ions in **1** has been rationalized by referring to the charge density distribution calculated for the disilirane adduct of $La_2@C_{80}$.[8]

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